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CONTRACT NUMBER: N68171-95-C-9067
PURCHASE REQUESTED NO.: WK2Q6C-7637-CH09
SECOND INTERIM REPORT RELATIVE TO THE
CONTRACT DELIVERY DATE: 09/01/95

*SUBJECT - IONICALLY CONDUCTING GEL POLYMER
ELECTRONICS*

Introduction

During this period the characterization of the previously reported first set of PAN-based gel electrolyte samples has been continued by determining the stability of lithium electrode /electrolyte interface as the compatibility with the electrode materials is an essential parameters to guarantee acceptable performance in electrochemical devices, especially when cyclability and reliability are considered.

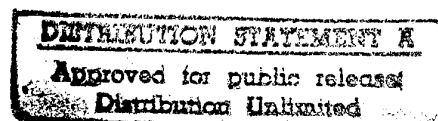
At the same time a second set of polymeric PMMA-based gel electrolyte samples, having the following molar compositions, have been prepared and characterized:

- 1) LiClO_4 4.5 / PC 19 / EC 46.5 / PMMA 30
- 2) LiAsF_6 4.5 / PC 19 / EC 46.5 / PMMA 30
- 3) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 4.5 / PC 19 / EC 46.5 / PMMA 30

These samples have been prepared following the preparative route later described in the text and characterized by determining their ionic conductivities, the cationic transference numbers and the electrochemical stability windows.

All the preparation procedures of the gel electrolytes and the related electrochemical measurements were carried out in an Argon filled glove box whose atmosphere had a moisture content constantly lower than 5 ppm.

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1) Stability of the lithium electrode/PAN-based gel electrolyte interface

1.1) Experimental

The Li/SPE (Solid Polymer Electrolytes) interfacial characteristics were obtained by monitoring the time dependence of the impedance (AC measurements) of symmetrical Li/SPE/Li cells utilizing a Solartron Mod. 1260 Frequency Response Analyzer.

1.2) Results and discussion

Figure 1 illustrates the time evolution of the interfacial resistance R_i of the lithium electrode in contact with different PAN-based gel electrolytes under open circuit condition (OCV) and at room temperature. The trend of R_i indicates that lithium metal electrode is passivated when in contact with PAN-based gel electrolytes. This behaviour is due presumably to the electrolyte components (such as PC and EC), which are lithium corrosive agents and form a thin passivation layer (usually a composite formed by inorganic - Li_2CO_3 , Li_2O , etc.- and organic - e.g. alkoxides - compounds) over the electrode surface. As previously discussed these components diffuse from the bulk of the gel electrolyte to reach the lithium interface, thus inducing the observed passivation effects.

The comparison of the interfacial resistance trend reveals that the rate of passivation is different, being fast at the initial stage to then becoming progressively slower.

Also the electrolyte salt may have a role in the passivation phenomena. The resistance of the gel electrolyte containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ has a different trend than the others PAN-based electrolytes one (see figure 1) and suggests that the passivation tends to reach a final constant level. On the contrary, the trends obtained for the LiClO_4 and LiAsF_6 -based electrolytes confirm that passivation occurs with a continuous growth of a resistive layer at lithium/SPE interface [1].

1.3) Conclusion

In summary, the impedance analysis indicates that passivation of the lithium electrode takes place in all the PAN-based gel electrolytes here examined. On the other hand, the type of passivation seems to vary from one electrolyte to another, suggesting a definite role of the electrolyte salt in controlling the phenomenon. Therefore, the selection of a proper solvent-salt-polymer combination may limit the extent of the passivation to assure acceptable stability of the interface and thus, good lithium cyclability.

2) PMMA-based gel electrolyte

2.1) Synthesis

The chemicals used in the preparations were adequately purified and dried. PMMA (Aldrich, reagent grade; average molecular weight of 996.000), lithium perchlorate (LiClO_4 , Fluka, high-purity grade) and trifluoromethanesulphone imide ($\text{LiN}(\text{CF}_3\text{SO}_2)$, 3M, high-purity grade) were dried, for at least 24 hours, under vacuum at 60, 110 and 80 °C, respectively. Similarly, the lithium hexafluoroarsenate (LiAsF_6 , 3M product) was dried under vacuum for 24 hours at 80°C. Ethylene carbonate (PC, Fluka high-purity grade) was dried with type 4A molecular sieves for 48 hours and then distilled under vacuum. Karl-Fisher titrations for both EC and PC indicated water content of less than 18 ppm.

The film preparation procedure consisted of three consecutive steps (see figure 2). Initially, the selected lithium salt (LiX) was dissolved in a solution formed by mixing PC and EC in the correct molar ratio.

The second gelation step consisted in the addition of the PAN powder to the PC/EC- LiX solution followed by the room temperature mixing of the slurry in order to ensure a good wetting of the PAN and its initial swelling. This step was completed by placing the pre-swelled mixture in a heated silicon oil bath at 100-120°C and by stirring until a clear viscous gel was formed. In the third final step the films were fabricated by casting the hot gels between spacers-furnished glass plates which allowed the samples thickness control.

Upon cooling at room temperature free-standing, very transparent, homogeneous, elastomeric films were formed.

2.2) Samples characterization

The characterization of the samples has consisted in determining the following three main electrochemical properties relevant to their exploitation in the field of lithium batteries, namely:

- the ionic electrical conductivity;
- the cationic transference number;
- the electrochemical stability window.

Electrical conductivities were determined from AC impedance measurements utilizing a Solartron Mod. 1260 Frequency Response Analyzer with a SS/SPE/SS cell configuration (SS= Stainless Steel).

Lithium ion transference numbers were measured utilizing the so-called 'time of fly' method described by Watanabe and co-workers.

The anodic decomposition potentials were determined by the use of a three-electrode cell with lithium as both counter and reference electrodes and nickel as working electrode.

2.3) Results and Discussion

2.3.1) Introduction

All samples showed a plastic-like physical consistency and were very transparent and uncoloured. Furthermore all films had, unlike the PAN-based SPE, no slightly wet surfaces due to the fact that all the solvent (PC and EC mixture) is interacting directly with the polymer chains [2].

2.3.2) Electrical conductivity

For all of the prepared samples the conductivity showed high values, around 7×10^{-4} S/cm 25°C (see Table 1). The electrical conductivity data are reported as the Arrhenius plots of figure 3. Throughout the entire temperature range of the measurements, the Arrhenius plots exhibit significant curvature, which is characteristic of Vogel-Tamman-Fulcher (VTF) behavior [3]. The ionic conductivity values of the three samples are similar, even if the differences are significant. By a regression analysis of the conductivity data on the VTF equation:

$$\sigma = A \cdot T^{1/2} \exp[-E_a / (T - T_0)]$$

performed by the use of a non-linear least square best fitting program, it has been possible to obtain the T_0 , A and E_a as fit-adjustable parameters. The three gels exhibited very similar values of E_a close to those usually found for the corresponding liquid solutions.

2.3.3) Anodic decomposition

Figure 4 shows the current voltage responses obtained for the three samples at room temperature. The trend of these curves suggests that the gel electrolyte containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ seems to be the most stable with the onset of the decomposition current reaching 4.9 V, even if it shows a small peak around 4.6 V. This phenomenon seems to suggest a partial dissociation of the $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ anion.

The gel sample containing the LiClO_4 electrolyte shows the lowest value of the anodic decomposition potential (see Table 1) lower than the corresponding PAN-based gel electrolyte. On the contrary the sample containing LiAsF_6 has a higher anodic decomposition potential value.

This is probably due to the different interactions of liquid electrolyte with PMMA and PAN polymeric chains (for example PMMA is not decomposed by the dissociation products of the $(\text{AsF}_6)^-$ because it has no α -hydrogen [see first interim report]).

2.3.4) Li^+ Transference Numbers.

Table 1 shows the Li^+ transference number values (t_{Li^+}) of the three PMMA-gel electrolyte samples obtained by the 'time of fly' method. These values are much higher than those usually reported for liquid and PEO-based polymer electrolytes. Although a high value of t_{Li^+} is a beneficial characteristic for gel electrolytes to be exploited in solid-state polymeric electrochemical devices, one has to be aware that the techniques used for the t_{Li^+} determination may be associated to a certain degree of uncertainty, specially in high concentrated solutions where the extent of ion-ion and ion-solvent association is unpredictable. Nevertheless, taking into account the qualitative character of the data relative to t_{Li^+} in Table 1, it is worth to note that the sequence of the values is logical since they increase in the same order of the increases of the size of the anions, namely $(\text{ClO}_4)^- > (\text{AsF}_6)^- > (\text{N}(\text{CF}_3\text{SO}_2)_2)^-$.

2.4) Conclusion

PMMA-based gel electrolytes have the prerequisites for their exploitation as electrolytic membranes in practical electrochemical devices [4]. In particular the high ionic conductivities, the elevated electrochemical stability windows and the satisfactory Li^+ transference numbers confer to these membranes the suitability for their use in the realization of lithium-based high energy density rechargeable batteries. Moreover, the PMMA-based gel electrolytes have shown a complete retention of the gelating solvents as the result of a good interaction between the polymeric chains and the solvent molecules. Therefore the surfaces of the films are not wetted and a lower reactivity with the lithium anode (of the batteries) is expected.

3) Future works

A) In the following period the lithium/PMMA-based gel electrolyte interface will be studied at the same operative conditions than the Li/PAN-based gel electrolyte one.

B) It will be started the preparation and the characterization of a new class of polyvinylidenedifluoride(PVDF)-based gel electrolytes.

References

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- [3] G. B. Appetecchi, F. Croce, B. Scrosati; *Electrochimica Acta*, 40 (1995) 991.
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Figure captions

Figure 1: Time evolution of the interfacial resistance R_i of the lithium electrode in contact with different PAN-based gel electrolytes respectively under open circuit condition and at room temperature.

Figure 2: Schematics of a PMMA-based gel electrolytes preparation.

Figure 3: Arrhenius plots of PMMA-based gel electrolytes.

Figure 4: Current-voltage response at 25°C of a nickel electrode in different PMMA-based gel electrolytes respectively. Scan rate: 1 mVs⁻¹. Lithium reference.

Table 1

Electrochemical properties of PMMA-based gel electrolytes at 25°C.

Electrolyte membrane	Conductivity [S$\text{cm}^{-1} \times 10^{-3}$]	Li⁺ transference number	Anodic stability [V] vs. Li⁺/Li
LiClO ₄ 4.5, PC 19 EC 46.5, PMMA 30	0.7	0.4	4.6
LiAsF ₆ 4.5, PC 19 EC 46.5, PMMA 30	0.8	0.6	4.8
LiN(CF ₃ SO ₂) ₂ 4.5, PC 19, EC 46.5 PMMA 30	0.7	0.7	4.9

Figure 1

Time evolution of the interfacial resistance R_i of the lithium electrode in contact with different LiX, PC:EC, PAN gel electrolytes under open circuit condition and at room temperature.

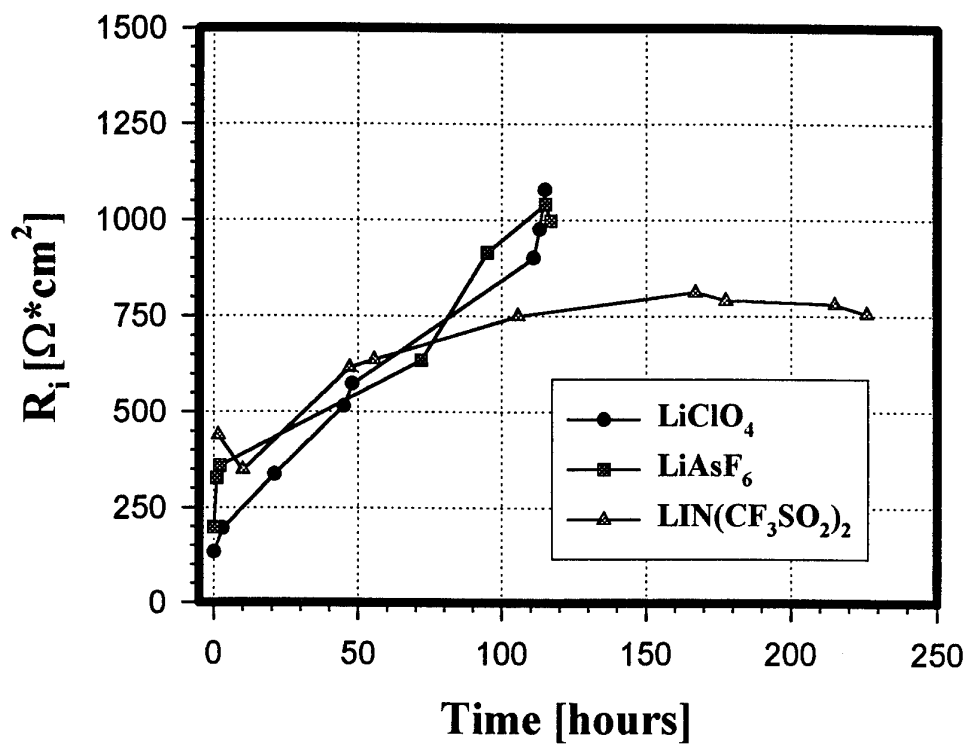


Figure 3

Arrhenius plots of PMMA-based gel electrolytes.

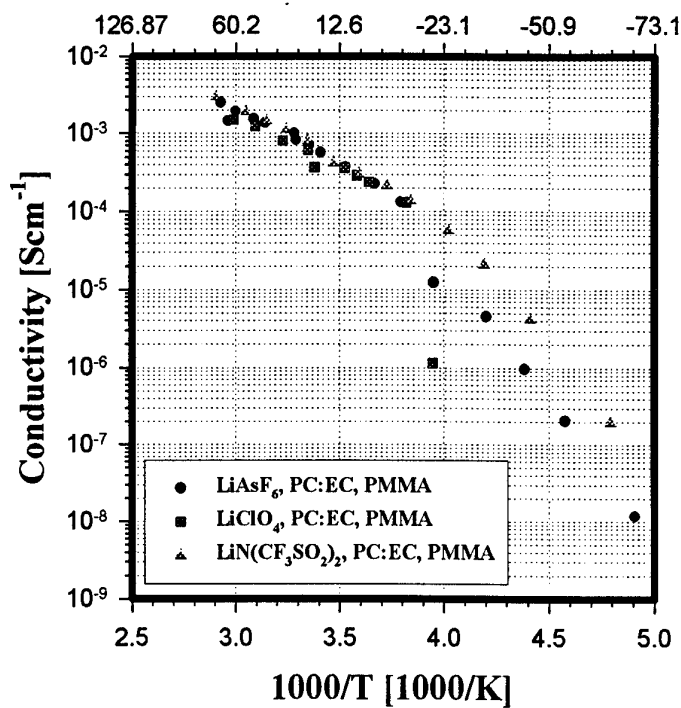
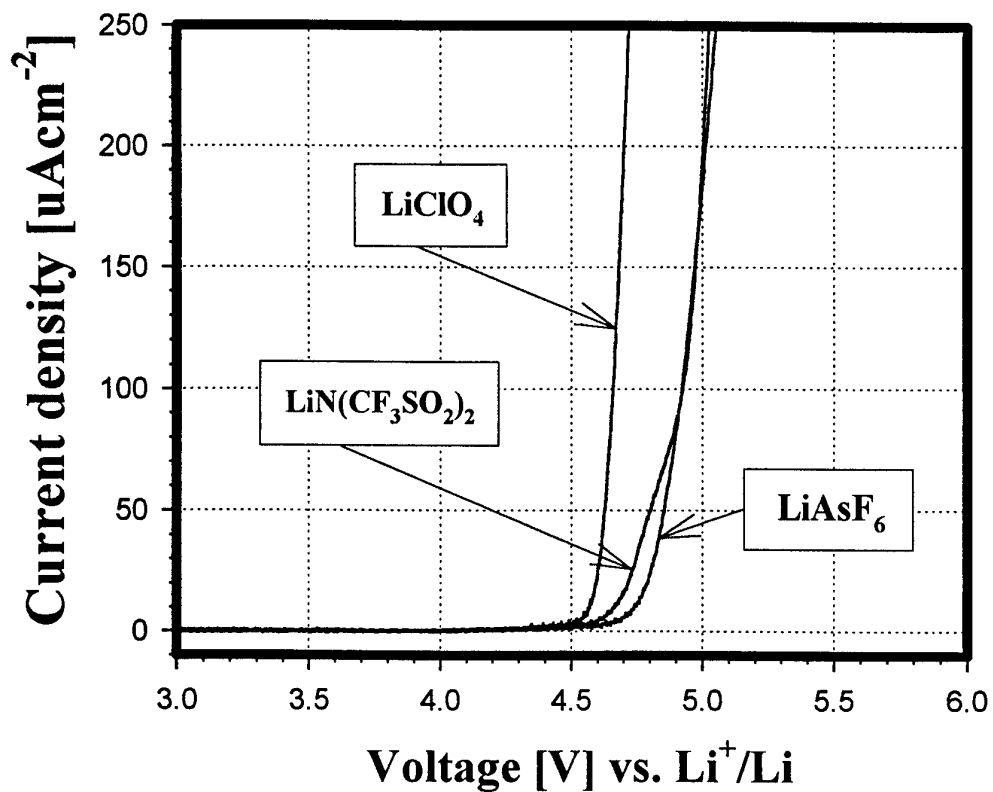


Figure 4

**Current-voltage response at 25°C of a nickel electrode
in different LiX, PC:EC, PMMA gel electrolytes.
Scan rate: 1 mVs⁻¹. Lithium reference.**



PREPARATION OF GEL-TYPE MEMBRANE

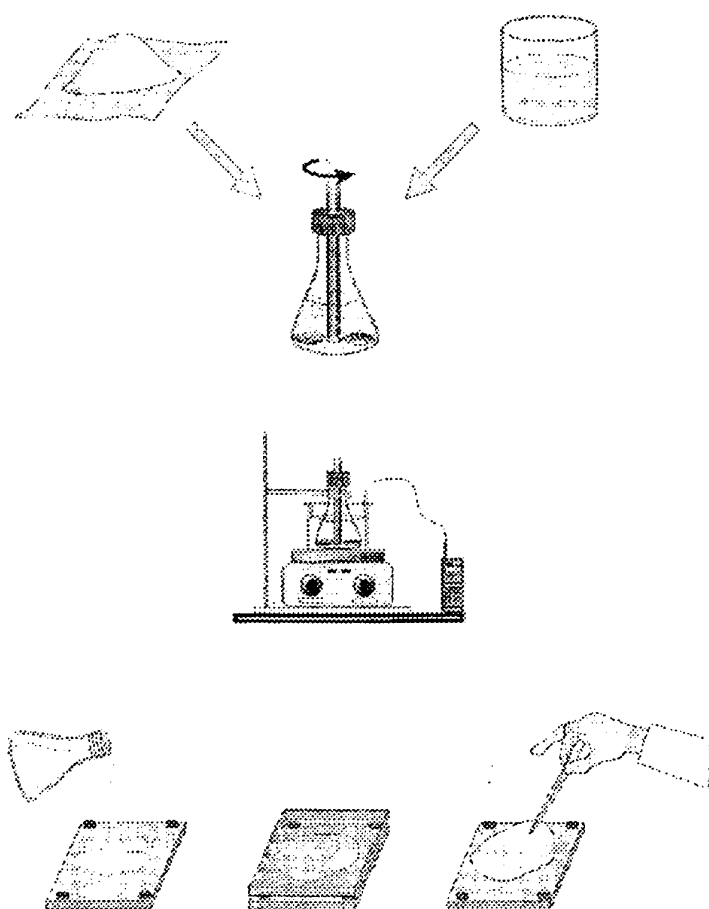


Fig. 2